PATENT COOPERATION TREATY

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From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

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NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing *(day/month/year)* 28.06.00

IMPORTANT NOTIFICATION

International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/NL99/00216	14/04/1999	15/04/1998

Applicant
NEDERLANDSE ORGANISATIE VOOR TOEGEPAST- NATUURWETE

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.

2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.

3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

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PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
P22286PC00		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/NL99/00216	14/04/1999	15/04/1998
International Patent Classification (IPC) or national classification and IPC C06D5/08		
Applicant NEDERLANDSE ORGANISATIE VOOR TOEGEPAST- NATUURWETE		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which hav been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 6 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☒ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
11/11/1999	28.06.00
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Werner, H Telephone No. +49 89 2399 8571

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL99/00216

I. Basis of th report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1	as originally filed			
2-5	as received on	20/03/2000	with letter of	20/03/2000

Claims, No.:

1-12	as received on	20/03/2000	with letter of	20/03/2000

Drawings, sheets:

1/1	as originally filed

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☒ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

see separate sheet

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with r gard to n velty, inventive step r industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims 1-12
	No:	Claims
Inventive step (IS)	Yes:	Claims 1-12
	No:	Claims
Industrial applicability (IA)	Yes:	Claims 1-12
	No:	Claims

2. Citations and explanations

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

SECTION I

The amendments filed with the letter dated 20.3.2000 introduce subject-matter which extends beyond the content of the application as filed, contrary to Article 34(2)(b) PCT. The amendments concerned are the following: In the amended claim 1 the composition comprises water and/or **a solvent**. However, "a solvent" has not been disclosed in the original application (on page 3, line 6, "an organic solvent" is disclosed").

SECTION V

The problem to be solved by the present application is to provide a monopropellant composition for spacecraft propulsion and other uses which is stable, of low toxicity, and of low flammability.
This problem is solved by the present application by a monopropellant composition comprising 25-95% hydrazinium nitroformate (HNF) and/or ammonium dinitramide (ADN) in water and/or a solvent.
This composition is liquid, stable and of low flammability and has a specific impulse equal to conventional monopropellants.

Documents cited in the international search report:
DATABASE COMPENDEX ENGINEERING INFORMATION, INC., NEW YORK, NY, US OXLEY J C ET AL: 'Thermal decomposition studies on ammonium dinitramide (ADN) and N and H isotopomers' XP002075366 & J PHYS CHEM A;JOURNAL OF PHYSICAL CHEMISTRY A JUL 31 1997 ACS, WASHINGTON, DC, USA, vol. 101, no. 31, 31 July 1997, pages 5646-5652 discloses the kinetics of decomposition of ADN in water.
US-A-5 316 749 discloses extracting ADN with ethanol and methanol.
WO 97 06099 A discloses preparation of ADN.
WO 94 10104 A discloses preparation of HFN.
AGRAWAL J P: 'Recent trends in high-energy materials' PROGRESS IN ENERGY AND COMBUSTION SCIENCE, vol. 24, no. 1, 1998, page 1-30 XP004107967 discloses technical data on ADN and HNF.
US-A-5 648 052 discloses a liquid propellant comprising water with no ADN or HNF
WO 91 19669 A discloses technical data on ADN.

CHEMICAL ABSTRACTS, vol. 123, no. 14, 2 October 1995 Columbus, Ohio, US; abstract no. 174351p, T. ANAN ET AL.: 'Physical and chemical properties of HNF' page 281; XP000663569 & KAYAKU GAKKAISHI, vol. 56, no. 3, 1995, pages 99-104 discloses and technical data on HNF.

The claimed invention is not derivable from the cited documents and therefore inventivity is justified.

SECTION VIII

Claim 1 is not supported by the description as required by Article 6 PCT, as its scope is broader than justified by the description. The reasons therefor are the following: The claimed monopropellant composition as described on page 2 comprises "water and/or **a lower alcohol**" whereas in claim 2 "water and/or **a solvent**" is claimed. Furthermore, "a lower alcohol" would contravene Art. 6 PCT since "lower" is a vague and undefined term (the subject-matter of claim 3, a" C1-C4 alkanol", would clarify the term "lower").

autodecomposition behaviour. Drawbacks of hydrazine are its toxicity and flammability.

These aspects of currently used monopropellants accordingly require high level, and thus costly, requirements for production, transport, storage, handling and disposal.

The same problems are encountered in emergency systems for jet fighters (emergency start-up of engine after flame-out) and submarines (emptying ballast tanks in emergency situation by generating gas).

It is one of the objects of the present invention to provide a monopropellant composition for spacecraft propulsion and the other uses described above, which obviates these drawbacks of the prior art system. It is a further object to provide a stable, clean, less toxic, and/or less flammable monopropellant composition. It is also an object to provide a monopropellant composition for spacecraft propulsion that could contribute to a relaxation of requirements and therefore to a reduction of costs and launch preparation time.

The present invention is based on the surprising finding that known solid high energy oxidisers such as hydrazinium nitroformate and ammonium dinitramide, when dissolved in water provide a liquid monopropellant system having a specific impulse that could be equal to the specific impulse of the conventional monopropellants, without having the disadvantages thereof.

The invention is accordingly directed to a solution of hydrazinium nitroformate and/or ammonium dinitramide in water and/or a lower alkanol as monopropellant composition, especially in spacecraft propulsion. The amount of water and/or lower alkanol in the system should be such that the system is liquid, which determines the lower level of the amount of water. On the other hand there should be sufficient hydrazinium nitroformate and/or ammonium dinitramide present

in the system to provide the required impulse. Accordingly, the amount of HNF and/or ADM is from 25 to 95 wt.% of the composition. Due to the nature of spacecraft propulsion, this specific impulse of the propellant system should be as high as possible, in order to prolong the lifetime of the satellite.

According to a preferred embodiment hydrazinium nitroformate in water is used. In another embodiment of the propellant system according to the invention additionally an amount of an organic solvent, for example a lower alkanol, such as methanol, ethanol, propanol or butanol, can be used. It has been found that this increases the specific impulse of the monopropellant. The amount of alkanol in the solution is preferably between 0 and 70 wt.%, whereas methanol and/or ethanol are preferred.

An especially preferred system consists of 25 to 75 wt.% of hydrazinium nitroformate, 5 to 50 wt.% of water and 0 (more preferred 5) to 25 wt.% of lower alkanol.

In accordance with the invention it is also possible to include other additives in the propellant system, including, but not limited to solubilisers, vapour pressure decreasing agents and performance improving agents.

In another embodiment the present invention is directed to a process for orienting and positioning of spacecraft after delivery into the required orbit by a launch vehicle using a spacecraft propulsion system based on monopropellant thrusters, wherein the monopropellant discussed hereinabove is used for propulsion.

Hydrazinium nitroformate and ammonium dinitramide are known high energy solid oxidisers. The use of hydrazinium nitroformate as ingredient in high performance propellant combinations for rocket engines is for example disclosed in European patent application 350,136. A production process for hydrazine nitroformate is further disclosed in the international patent application WO-A 9410104. Ammonium dinitramide is also a known material, the production of which is for example disclosed in WO-A 9424073.

The monopropellants according to the invention can be used in the conventional way for spacecraft propulsion, in existing systems, whereby it is to be noted that due to the properties of the system, less strict requirements concerning storage, transport and handling are possible. Also the use of the monopropellant system as emergency propellant in jet fighters and emergency gas generation systems for submarines is within the scope of the present invention.

Description of the figure.

The figure shows a comparison of specific impulse of various propellant systems.

The specific impulse of various monopropellant systems in accordance with the invention has been compared with the values for an aqueous solution of ammonium dinitramide and hydrazinium nitroformate in water, at 50 wt.% water. In the following table and in the figure the specific impulse is given for an expansion ratio of 50 and a chamber pressure of 1 MPa, zero ambient pressure and at chemical equilibrium outflow conditions.

Table 1

Ingredient	Specific Impulse m/s Based on 50% water and 50% oxidiser	For the pure oxidiser
Hydrazinium Nitroformate (HNF)	1754	2950
Ammonium Dinitramide (ADN)	1267	2319
Hydrogen Peroxide (H_2O_2)	1872	
Hydrazine (N_2O_4)	2266	

AMENDED SHEET

As can be seen in the table 50% oxidisers/water mixtures result in a performance loss compared to hydrogen peroxide and hydrazine. This performance loss may be acceptable in view of the reduction of cost due to simpler procedures for production, transport, storage, handling and disposal. Furthermore, by increasing the amount of dissolved oxidiser the performance can be further increased. If fuels such as lower alkanols are added, performance equal to or even exceeding the performance of hydrazine is possible.

In the attached figure the specific impulse is given for various compositions of hydrazinium nitroform in water, using various concentrations, ammonium dinitramide in water using various concentrations and for a combination of hydrazinium nitroform, ethanol and water.

AMENDED SHEET

VEREENIGDE OCTROOIBUREAUX
'S-GRAVENHAGE (HOLLAND)

Int.pat.appln.PCT/NL99/00216
our letter of March 20, 2000

Hz/RL P22286PC00

New claims

1. Monopropellant composition for propulsion and/or gas generation, comprising a solution of hydrazinium nitroformate (HNF) and/or ammonium dinitramide (ADN) in water and/or a solvent, and wherein the amount of HNF and/or ADN is from 25 to 95 wt.% of the composition.

2 Monopropellant composition according to claim 1, comprising water and an amount of a solvent.

3. Monopropellant composition according to claim 2, wherein the solvent is an alkanol, preferably a C_1-C_4 alkanol.

4. Monopropellant composition according to claim 3, wherein the alkanol is methanol and/or ethanol.

5. Monopropellant composition according to claim 3 or 4, wherein the amount of alkanol is at most 70 wt.%.

6. Monopropellant composition according to claims 1-5, consisting of 25 to 75 wt.% of hydrazinium nitroformate, 5 to 50 wt.% of water and 0 to 25 wt.% of lower alkanol.

7. Monopropellant composition according to claims 1-6, further comprising solubilisers, vapour pressure decreasing agents and/or performance improving agents.

8. Use of a composition of hydrazinium nitroformate and/or ammonium dinitramide according to claims 1-7 as propellant in spacecraft propulsion.

9. Use of a composition of hydrazinium nitroformate and/or ammonium dinitramide according to claims 1-7 as emergency propellant in jet fighters.

10. Use of a composition of hydrazine nitroformate and/or ammonium dinitramide according to claims 1-7 in an emergency gas generation system for submarines.

AMENDED SHEET

11. Process for orienting and positioning of spacecraft after delivery into the normal orbit by a launch vehicle by the use of spacecraft propulsion system based on monopropellant thrusters, wherein the monopropellant according to claim 1-7 is used for propulsion.

12. Use of a composition comprising a solution of HNF and/or ADN for propulsion and/or gas generation.

AMENDED SHEET